Letter to the Editor

SO$_x$ storage and release kinetics for ceria-supported platinum

1. Introduction

Energy-efficient solutions for propulsion within the transportation sector are likely to involve oxygen excess (lean) combustion [1]. A possible concept to reduce the NO$_x$ levels in the resulting (net-) lean exhausts is NO$_x$ storage catalysis (NSC) [2]. However, the NSC has a high affinity towards sulfur oxides (SO$_x$) which poison the storage sites and lead to severe deactivation. Thus, the NSC should not be exposed to even small amounts of SO$_x$ originating from fuels and/or lubricants. It is challenging to find appropriate solutions to this durability issue as emission standards need to be fulfilled over an expected useful period [3].

Strategies to prevent deactivation have been proposed where the NSC formulation is modified to include a SO$_x$ trapping materials that can store and release SO$_x$ under lean and rich conditions, respectively [4,5]. Another concept to hinder SO$_x$ from reaching the NSC is to add a, so-called, sulfur trap upstream the NSC in the aftertreatment system [6–11]. Two different types of sulfur traps have been proposed, i.e., disposable and regenerable. Here, the latter is considered to be used under continuously lean conditions.

In a previous study [11] it has been found that for continuously lean conditions, CeO$_2$-based materials are suitable for regenerable SO$_x$ traps. The design target in this case was to store SO$_x$ by adsorption below 500 °C and release stored SO$_x$ by thermal desorption above 600 °C. The addition of platinum was measured to significantly enhance the SO$_x$ storage. However, the actual role of platinum was not clarified although various scenarios were discussed including the importance of SO$_2$ oxidation and spill-over of SO$_x$ species. In the present work, the influence of SO$_2$ oxidation and noble metal–support interaction on SO$_x$ adsorption and desorption kinetics for Pt/CeO$_2$ is studied in more detail.

2. Experimental

2.1. Sample preparation and characterization

The supported platinum samples were prepared by impregnating ceria and silica, respectively, with halogen-free platinum precursors. Ceria (99.5 H.S.A. 514, Rhône-Poulenc) was dispersed in distilled water and an aqueous solution of platinum(II)nitrate (Pt(NO$_3$)$_2$, Heraeus GmbH) was gently added to the ceria slurry under continuous stirring. The slurry was, thereafter, instantly frozen with liquid nitrogen and freeze-dried. The resulting powder was calcined in air at 600 °C for 1 h (heating rate of 4.8 °C/min from 25 to 600 °C). The corresponding procedure was used to prepare the Pt/SiO$_2$ sample by impregnating colloidal silica (20 nm spherical particles, Nyacol 2034DI, Eka Chemicals) with an aqueous solution

of tetraammineplatinum(II)nitrate (Pt(NH$_3$)$_4$(NO$_2$)$_2$, Degussa AG). The platinum load was for both catalysts 5% by weight.

Four types of monolith samples were prepared by immersing bare cordierite monoliths ($\varnothing$ = 20 mm, length = 18 mm, 400 cpsi) in water slurries containing a binder and, respectively, Pt/CeO$_2$, Pt/SiO$_2$, CeO$_2$ and SiO$_2$ material. A colloidal ceria sol (10–20 nm spherical particles, Nyacol CeO$_2$(Ac), Nyacol Nano Technologies) and colloidal silica sol (20 nm spherical particles, Nyacol 2034DI, Eka Chemicals) was used as a binder for the ceria and silica materials, respectively. The coated monolith samples were then dried in air at 90 °C for 2 min and calcined at 600 °C for 5 min also in air. By repeating this procedure, 1 g of the respective coating was attached to each sample. All samples were calcined in air at 600 °C for 90 min and stabilized in a mixture of 1% CO, 0.15% C$_3$H$_8$ and 2% O$_2$ (Ar as balance) using a total flow of 3000 ml/min.

2.2. SO$_x$ adsorption and desorption experiments

The adsorption and desorption experiments were carried out using a gas-flow reactor described elsewhere [11]. Briefly, it consists of a horizontal quartz tube surrounded by a metal coil for resistive heating of the gas flow and the samples. Gases are introduced via individual mass flow controllers and the gas temperature in front of the sample is controlled by a Eurotherm regulator. The reactor is equipped with a Fourier transform infrared spectrometer instrument (MultiGas 2030, MKS Instruments) for simultaneous detection of gas phase SO$_2$ and SO$_3$ in the outlet stream.

The investigated sample configurations, depicted in Fig. 1, were evaluated by lean SO$_x$ adsorption (100 vol.-ppm SO$_2$ and 7% O$_2$ in Ar) at 250 °C for 1 h followed by a lean temperature programmed desorption (7% O$_2$ in Ar) by ramping the temperature from 250 to 700 °C with a ramp rate of 10 °C/min. The total flow was in both cases 3500 ml/min. This adsorption–desorption sequence was repeated three times.

3. Results and discussion

In a previous investigation with the same conditions as the ones used here [11], it was observed that fresh ceria based SO$_x$ traps exhibit a certain degree of irreversible adsorption. In the present study, the same lean SO$_x$ adsorption–desorption sequence was carried out three times so as to obtain regenerable and reproducible results. As the basis for the discussion we use here only the second and third sequence.

In Fig. 2, the results for lean SO$_x$ adsorption (third sequence) on the different sample configurations A–D are shown. In the following discussion we assume that the SO$_2$ adsorption on SiO$_2$ and Pt/SiO$_2$ is negligible. This has been shown in several previous studies [12,13]. It is clear that the adsorbed amount of SO$_x$ is much higher for the Pt/CeO$_2$ sample (A) as compared to bare CeO$_2$ (D).
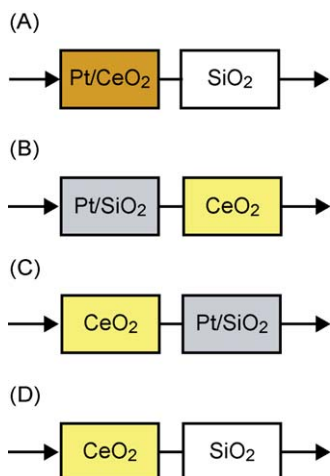
Fig. 1. Schematic picture of the four (A–D) pairwise configurations 5%Pt/CeO$_2$, 5%Pt/SiO$_2$ and bare CeO$_2$ and SiO$_2$ monolith samples used to study SO$_x$ adsorption and desorption kinetics.
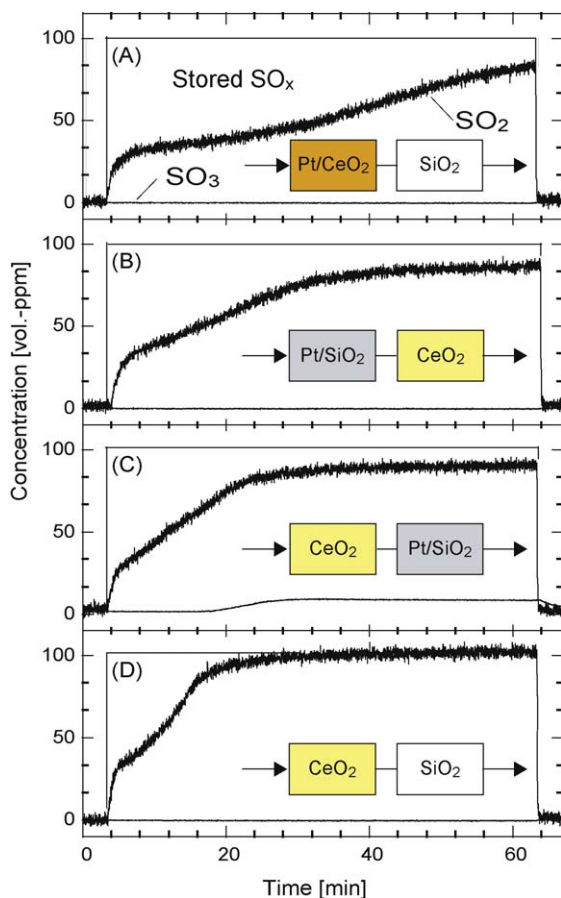

Fig. 2. Outlet SO$_2$ and SO$_3$ concentration traces during lean SO$_x$ adsorption (100 vol.-ppm SO$_2$/7%O$_2$/N$_2$) at 250 °C for different sample configurations.

Note that the A geometry is not even saturated during the time frame of the experiment. Based on the second and third adsorption sequence, the average amount of adsorbed SO$_x$ is 406 and 106 μmol for the Pt/CeO$_2$ and CeO$_2$, respectively. This is in accordance with previous observations [11] which were connected to different routes whereby SO$_x$ adsorbs on Pt/CeO$_2$ and bare CeO$_2$, respectively. However, based on previous results it is not clear whether the increased SO$_x$ adsorption is thanks to the formation of gaseous

SO$_3$ over Pt and subsequent adsorption of SO$_3$ on ceria or if SO$_3$ (or some other sulfur species) is transported from the platinum crystallites to ceria via surface diffusion and spill-over processes. Similarly, diffusion and spill-over of oxygen to ceria may be important steps. To study the influence of sulfur carrier, here SO$_2$ and SO$_3$, on the SO$_x$ storage, we use as a starting point for the analysis the comparison of present results for SO$_x$ adsorption for the systems with physically separated platinum, *i.e.*, configurations B and C. These results are in turn compared with the Pt free system (configuration D).

It is found that the amount of adsorbed SO$_x$ on ceria is higher in the case of the Pt/SiO$_2$ positioned upstream of the ceria (configuration B) as compared to either the downstream position (configuration C) or, even more clearly, the configuration D without Pt. For configuration B, SO$_x$ is adsorbed during the entire 60 min period of SO$_2$ exposure, although the SO$_x$ adsorption is minor at the end of the period, as reflected by increasing concentration of outlet SO$_2$. The average amount of adsorbed SO$_x$ is 286 μmol. Contrary, for configuration C, the outlet SO$_2$ concentration reaches a steady level at about $t = 40$ min. The total SO$_x$ concentration (sum of SO$_2$ and SO$_3$) is close to the inlet SO$_2$ concentration of 100 vol.-ppm which indicates negligible SO$_x$ adsorption at the end of the measurement. Here the average adsorbed amount of SO$_x$ is 174 μmol. Similarly, for bare ceria (D) the outlet SO$_2$ concentration reaches a steady level even earlier at about $t = 30$ min.

The main difference in SO$_x$ adsorption between configuration B and C is likely owing to the different SO$_2$ oxidation kinetics for Pt and CeO$_2$. Provided that the gas phase concentration of SO$_3$ is sufficiently stable (this assumption is supported by thermodynamic calculations)[1], the present results support the earlier suggestion in Refs. [11,14] that oxidation of SO$_2$ into SO$_3$ over Pt is important for the overall SO$_x$ adsorption. At the temperature used here, the SO$_2$ oxidation and subsequent sulphate formation on bare ceria are slow [11]. Based on results for configuration B and C, a few scenarios can be envisioned as depicted in Fig. 3. For example, given that SO$_2$ and SO$_3$ compete for the same adsorption sites on ceria (scenario I versus scenario II), the present results indicate that SO$_3$ adsorption is kinetically favored. Another explanation could be that the additional SO$_x$ adsorption observed for configuration B occurs solely via the formation of SO$_3$ thanks to specific adsorption sites for SO$_3$ on the ceria.

Consider again the SO$_x$ adsorption onto the Pt/CeO$_2$ sample. Likely, the observed high adsorption is only partly explained by the formation of gaseous SO$_3$. The comparison with the corresponding results for physically separated Pt and ceria (configuration B) shows the Pt/CeO$_2$ adsorbs significantly more SO$_x$. Assuming that the rate of SO$_2$ oxidation into gaseous SO$_3$ is not too different in the two cases (this is supported by the fact that the same amount of Pt was used in both cases) and that SO$_3$ is sufficiently stable in gas phase, the ceria is in both cases exposed to similar gas composition. Thus, the results indicate that physical contact between platinum and ceria is important for the overall SO$_x$ adsorption process. Although the mechanistic details are difficult to deduce from the present results, we may speculate on different scenarios. If SO$_3$ is not stable in the gas phase under the conditions used here, then SO$_2$ oxidation close to the ceria is important (scenario III). However, as mentioned above, SO$_3$ is probably stable enough and, thus, a scenario where the SO$_3$ formed on Pt may diffuse on the Pt surface and spill-over to ceria (scenario IV) is possible. The SO$_3$ adsorbed on the ceria may then continue to diffuse on the ceria

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[1] In an atmosphere with oxygen excess (here the concentration of O$_2$ was 700 times that of SO$_2$), SO$_3$ is the thermodynamically favored SO$_x$ species at low temperatures. The equilibrium temperature for the composition 50% SO$_2$/50% SO$_3$ is 675 °C.
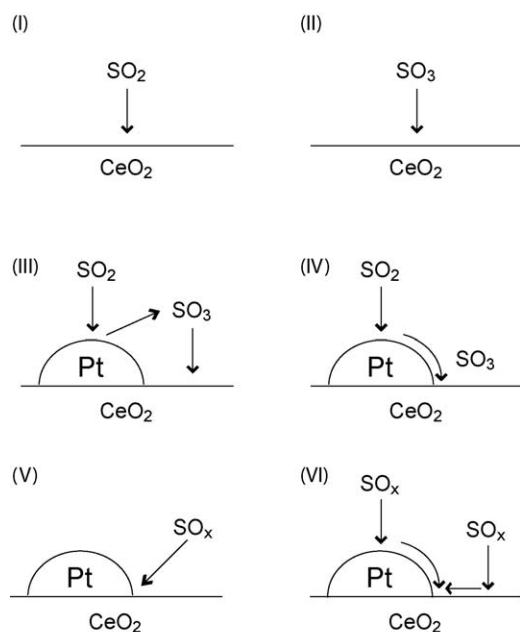
Fig. 3. Schematic picture showing possible routes for adsorption of SO_x on bare ceria and platinum–ceria systems.

surface as well as into the ceria bulk as was indicated by previous IR spectroscopy experiments [11]. In this case, the corresponding activation barriers for spill-over and diffusion are lower than the energy required for desorption. An expected crucial parameter in this respect is the length of the circumferential Pt–ceria interface. Another scenario that also involves the Pt–ceria interface as an important parameter, is the assumption of specific adsorption sites at the interface accessible for SO_x either directly from gas phase (scenario V) and/or via the platinum or ceria surface (scenario VI).

Hitherto it has been shown that the inclusion of Pt, preferable in direct contact with ceria, enhances the overall SO_x adsorption on ceria. Turning to the corresponding results for lean SO_x desorption (Fig. 4), the role of Pt is not as pronounced. One obstacle for the interpretation of the results is that for the four geometries the total amount of stored SO_x is different. This may influence the SO_x desorption spectra, especially the peak SO_x desorption. However, despite this issue, a few remarks can be made. The SO_x desorption starts at about 500 °C for all samples indicating that thermal decomposition of SO_x adsorbed on ceria is important for the release process. Furthermore, comparing configuration A and C the peak SO_x desorption occurs at a temperature only about 20 °C higher for Pt/CeO$_2$. This indicates that physical contact between Pt and ceria has a minor influence on the desorption and that, again, thermal decomposition of SO_x adsorbed on ceria is the main route. The present results differ from our previous study [11] where SO_x desorption occurred at higher temperatures for ceria samples without Pt. The reason for this is probably due to different sample preparation in the two studies. In the previous study, ceria was attached to monoliths using Boehmite as a binder. During sample calcination Boehmite forms alumina which is known to store SO_x also at relatively high temperatures [11]. Thus in the case of the ceria sample where a low amount of SO_x was stored, SO_x desorbed from ceria at low temperatures could be temporarily adsorbed on the alumina until higher temperature was reached. In the case of Pt/CeO$_2$, this effect is likely negligible due to the much higher amounts of stored SO_x. In the present study a ceria sol was used instead of Boehmite in order to prepare ceria samples with as few components as possible. It should be noted, however, that an indirect effect of Pt on the SO_x release kinetics for platinum–ceria systems could be observed in the present results. The desorption
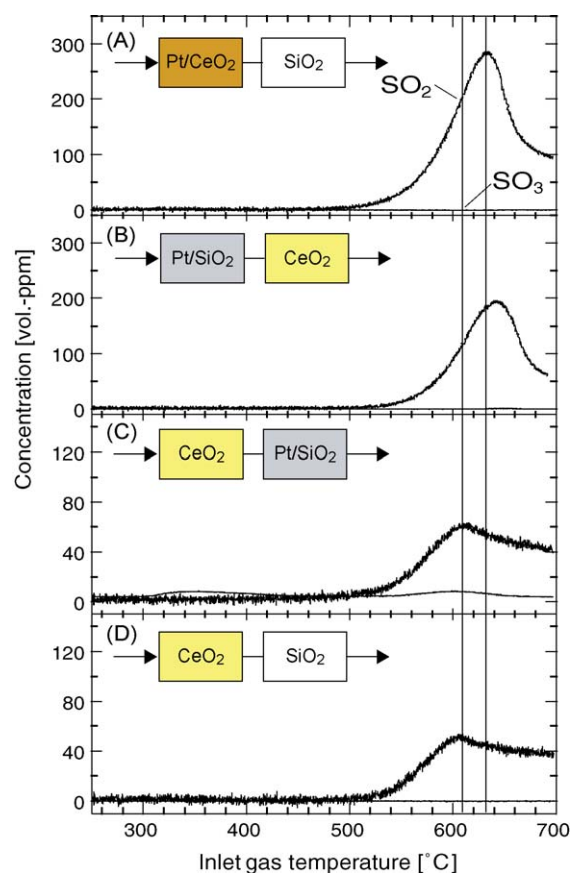

Fig. 4. Outlet SO_2 and SO_3 concentration traces during lean temperature programmed desorption of SO_x (7% O_2/N_2) for different sample configurations. Ramp rate 10 °C/min. The two vertical lines show the SO_2 peak desorption for configuration A and C, respectively.

spectra for configuration A and B as well as for C and D are similar. For A and B, SO_x was stored mainly via SO_3 adsorption, whereas for C and D, storage proceeds mainly via SO_2 adsorption. Adsorption of SO_3 leads preferably to formation of SO_4 species whereas SO_2 adsorption initially leads to formation of SO_3 species in the ceria structure [11]. This indicates that the route for SO_x adsorption is important for the corresponding desorption and, thus, inclusion of platinum has an indirect effect on the SO_x release kinetics for platinum–ceria systems.

4. Concluding remarks

In summary, we have shown that lean SO_x storage on platinum–ceria systems occurs both via adsorption of SO_2 and SO_3, where the latter is kinetically favored. Thus, the rate of SO_2 oxidation is important for the overall SO_x storage kinetics. Moreover, physical contact between platinum and ceria is important for the overall SO_x storage kinetics possibly by providing new transport routes (diffusion and spill-over) and/or adsorption sites at the platinum–ceria interface for SO_x. Thermal decomposition of SO_x species seems to be the main route for SO_x desorption and thus platinum plays a minor role. However, platinum may play an indirect role as the route for SO_x storage, *i.e.*, via SO_2 or SO_3 adsorption, seems to influence the SO_x desorption kinetics.

References

[1] S. Matsumoto, Cattech 4 (2001) 102.
[2] N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, K. Yamazaki, K. Yokota, H. Suzuki, N. Miyoshi, S. Matsumoto, T. Tanizawa, T. Tanaka, S.-s. Tateishi, K. Kasahara, Catal. Today 27 (1996) 63.
[3] http://www.dieselnet.com.
[4] J.H. Kwak, D.H. Kim, J. Szanyi, C.H.F. Peden, Appl. Catal. B: Environ. 84 (2008) 545.
[5] Y. Ji, T.J. Toops, M. Crocker, Catal. Lett. 127 (2009) 55.
[6] H.L. Fang, J.C. Wang, R.C. Yu, C.Z. Wan, K. Howden, SAE technical paper series 2003-01-3245.
[7] L. Limousy, H. Mahzoul, J.F. Brilhac, P. Gilot, F. Garin, G. Maire, Appl. Catal. B: Environ. 42 (2003) 237.
[8] H. Dathe, A. Jentys, J.A. Lercher, Phys. Chem. Chem. Phys. 7 (2005) 1283.
[9] L. Li, D.L. King, Ind. Eng. Chem. Res. 44 (2005) 7388.
[10] K. Tikhomirov, O. Kröcher, M. Elsener, M. Widmer, A. Wokaun, Appl. Catal., B: Environ. 67 (2006) 160.
[11] L. Kylhammar, P.-A. Carlsson, H. Härelind Ingelsten, H. Grönbeck, M. Skoglundh, Appl. Catal. B: Environ. 84 (2008) 268.
[12] T. Wang, A. Vazquez, A. Kato, L.D. Schmidt, J. Catal. 78 (1982) 306.
[13] E. Xue, K. Seshan, J.R.H. Ross, J. Catal. 11 (1996) 65.
[14] M.Y. Smirnov, A.V. Kalinkin, A.V. Pashis, A.M. Sorokin, A.S. Noskov, K.C. Kharas, V.I. Bukhtiyarov, J. Phys. Chem. B. 109 (2005) 11712.

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